Geochemistry of thirteen Voronin Trough cores, Kara Sea, European Arctic: Hg and As contaminants at a 1965 timeline

Frederic R. Siegel [a,*], Jennifer J. Galasso [b], Joseph H. Kravitz [c]

[a]*Geology, George Washington University, Washington, DC 20052, USA*
[b]*Naval Research Laboratory, Washington, DC 20375, USA*
[c]*Office of Naval Research, Arlington, VA 22217, USA*

Abstract

The potentially toxic elements Hg and As are found at high concentrations in surface/near-surface sediments from Arctic ocean cores collected from the Voronin Trough, Kara Sea, during 1965. The levels reach 2045 ppb for Hg and 270 ppm for As. Manganese high values (up to 1.27%) are also found in the cores' surface/near-surface sections. Other heavy metals tracked by the Arctic Monitoring and Assessment Program (e.g., Cu, Ni, Pb, Sb, Ti, Zn) have baseline concentrations in the cores. The cores average > 57% clay-size and > 35% silt-size in their textural composition. The elevated contents may result from anthropogenic input for Hg and As with diagenesis adding to the As concentration. Possible sources for these elements are emissions and effluents from industry such as mining and smelting operations, and burning of fossil fuels in Siberia and the Urals. When discharged into the Kara Sea from Siberian catchments, the As and Hg likely attach to charged particulate surfaces of Fe oxy/ hydroxides (for As) and particulate organic matter or clay minerals (for Hg). These are transported, entrained in ocean currents or adhered to pack ice, to the Voronin Trough where they deposit according to size and specific gravity. © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

Much of the focus on potential pollutants in the Arctic seas is on radioactivity. This is the result of the Yablokov et al. (1993) report of radioactive waste dumping from the middle 1950s–1991 in the SW Kara Sea off the Novaya Zemlya archipelago, the main Soviet nuclear arms testing facility, and in the SE Barents Sea. Included were liquid wastes, containerized solid wastes, and 13 atomic submarine sections plus one atomic icebreaker section, carrying 16 naval reactors, 6 with unspent fuel. Reactors were encapsulated in furfurol resin which is projected to isolate them from sea water for 500 a. Industrial support for the arms testing came from atomic complexes in the Urals and in Siberia (e.g., Chelyabinsk, Sverdlovsk, Omsk, Novosibirsk, Krasnoyarsk).

Emissions from fossil fuel burning electrical power plants, and emissions and effluents from industrial

* Corresponding author. Fax: +1-202-994-0450.
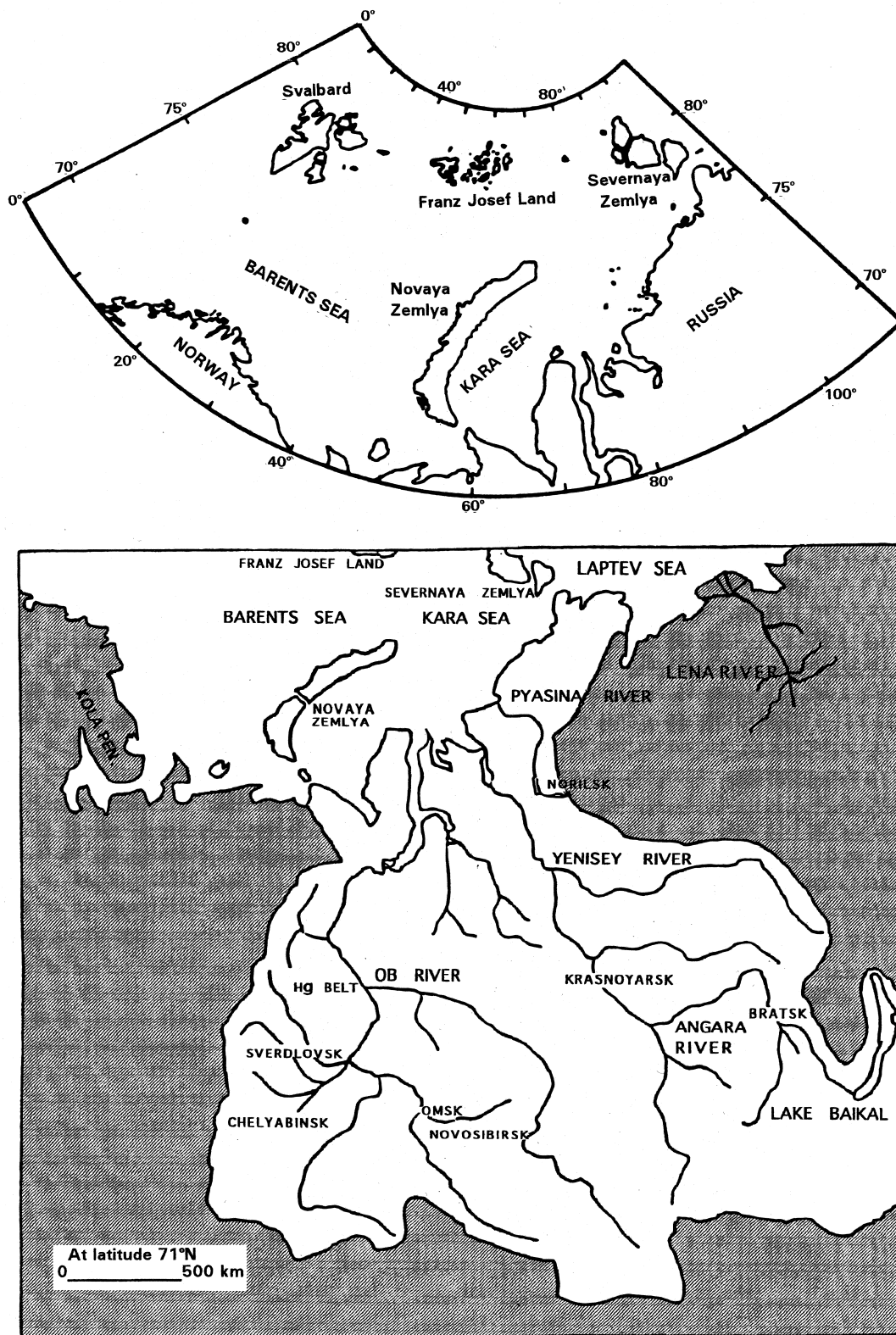*E-mail address:* nzkara@research.circ.gwu.edu (F.R. Siegel).

Fig. 1. Map showing the European Arctic with the Kara Sea and proximate land masses and drainage basins (compiled from Pavlov and Pfirman, 1995, and Naidu et al., 1975).

complexes, mine waste drainage, and smelting and mineral processing were sources of potentially toxic elements (Yablokov, 1996) that entered the catchments of the Ob and Yenisey rivers and discharged into the Kara Sea (Fig. 1). Military materials dumped in the Kara Sea are other possible sources for pollutants in the environment.

Galasso et al. (2000) reported high concentrations of Hg and As in eight Novaya Zemlya Trough cores collected in 1965. Arsenic contents reached 240 ppm vs a baseline of 20 ppm. Mercury contents were as high as 875 ppb vs a baseline of 338 ppb. The high As and Hg levels were considered to be contaminants from mining and smelting, industrial activity that supported the nuclear weapons testing program, ocean dumping of military materials, and fossil fuel burning, and with some As input from diagenesis. Contamination originated as emissions
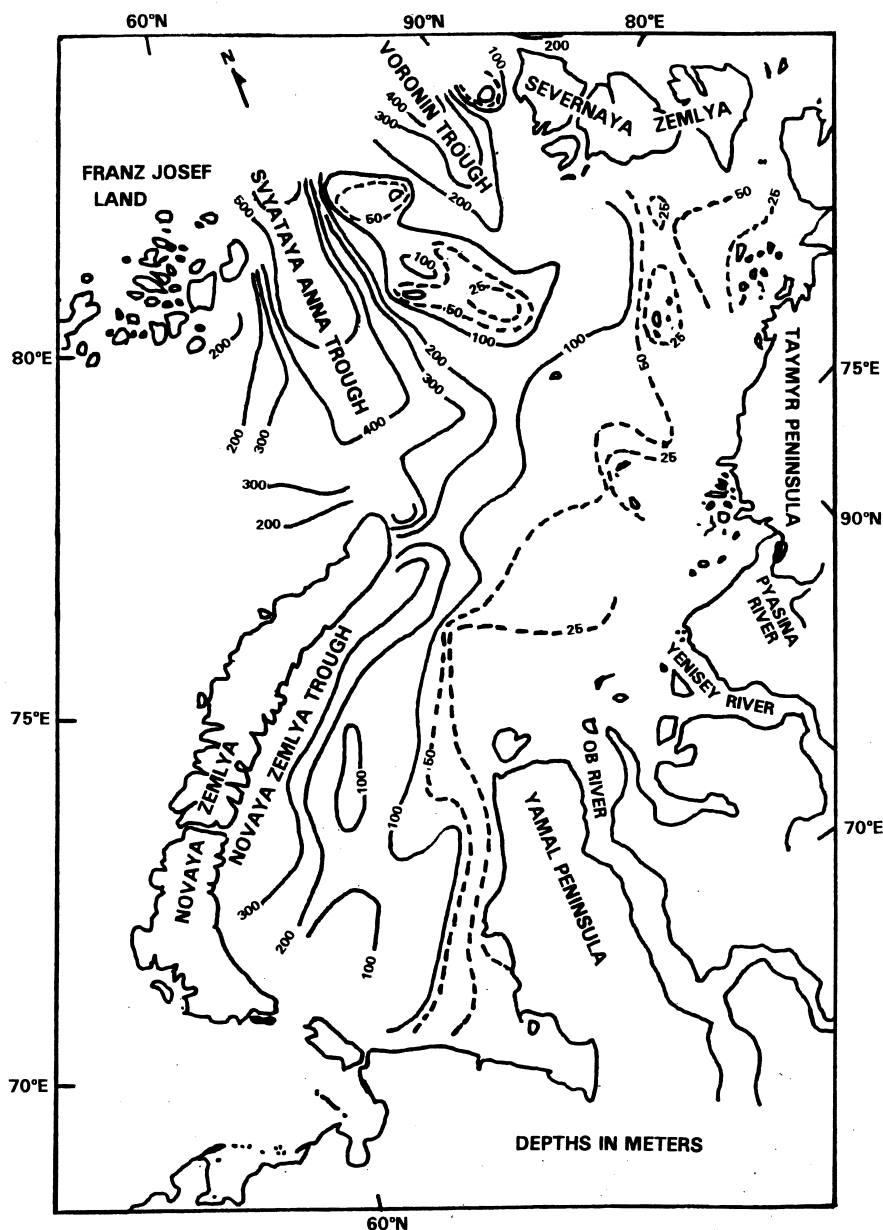

Fig. 2. Bathymetric map of Kara Sea showing locations of the Novaya Zemlya, Voronin and St. (Svyataya) Anna Troughs.

and effluents in the drainage basins emptying into the south Kara Sea from the Novaya Zemlya archipelago and Siberia. Input from the Kola Peninsula may have added to the As and Hg loading.

Marine circulation due to currents, and sea ice following flowpaths from areas of Siberian discharge may carry contaminants for deposition in the Voronin Trough. Cores collected from the Trough in 1965 (Andrew and Kravitz, 1974) are evaluated in the present study to determine if there was As and Hg contamination, and if so, at what concentrations over background. Another objective is to define the distribution of Hg and As in and among cores in order to evaluate in-core processes (e.g., diagenesis and bioturbation) that can affect element distribution and indicate probable sources and pathways to depositional sites. The data given here provide a 1965 geochemical timeline. Analysis of cores taken thereafter can show if contamination has increased or decreased or remained the same with respect to 1965 and whether other heavy metals subsequently reached values significantly exceeding 1965 baseline concentrations.

2. Drainage into the Kara Sea and impact on the Voronin Trough

The Voronin Trough is the smallest of 3 troughs in the Kara Sea (Fig. 2). At the 200 m isobath it covers 20,000 km^2 and has a maximum depth that exceeds 500 m. In comparison, the Novaya Zemlya Trough encloses an area of 60,000 km^2 with a maximum depth of more than 500 m whereas the St. (Svyataya) Anna Trough extends over 140,000 km^2 and has a maximum depth of approximately 640 m. The Voronin Trough is separated from the Novaya Zemlya Trough to the south by a sill at 100 m and from the St. Anna Trough to the SW by a sill which rises from 100 m depth to 50 and 25 m in some areas.

The principal discharge into the Kara Sea is from the Ob and Yenisey catchments that drain vast areas
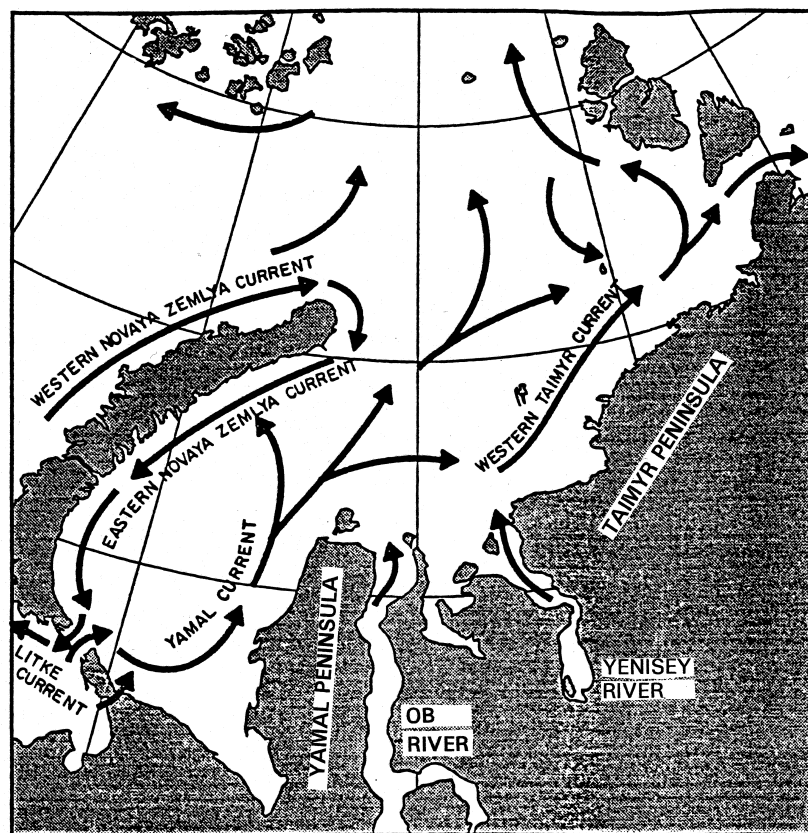

Fig. 3. Surface current flowpaths in the Kara Sea (Pavlov and Pfirman, 1995) and relation to surface/near-surface samples' high values for Hg and As in Voronin Trough cores.

of Siberia and the eastern Urals (Fig. 1). The Ob river annual discharge of 13.4×10^6 tons of suspended load is moved in great part by current activity to the NW into the counterclockwise gyre in the southern Kara Sea (Fig. 3). A lesser load moves into the Western Taimyr Current where it can influence Voronin Trough sediments. Farther to the north and east, the 14.5×10^6 tons of suspended sediment annual discharge from the Yenisey river joins the Western Taimyr Current and contributes to the sediments deposited in the Voronin Trough (Pfirman et al., 1995; Telang et al., 1991). North of the Yenisey, the Pyasina river (Fig. 1) which includes the atmosphere polluting Norilsk smelters in its drainage basin, discharges about 1.1×10^6 tons of suspended sediment yearly into the central Kara Sea. Much of this likely enters the Western Taimyr Current and adds to the sediment load in the Voronin Trough.

3. Methodology

3.1. Sampling

Thirteen Kullenberg gravity cores were collected from the Voronin Trough during August–September 1965 using the US Coast Guard Cutter Northwind as the sampling platform. Latitude–longitude data, core lengths, and sampling depths are given in Table 1. Samples were collected in plastic (Tulox) liners, capped, covered with plastic wrap, and sealed in wax. In accordance with the primary mission of the cruise, mass physical properties were measured on core sections separated by changes in lithology 4 months later. In addition, C_{org} was analysed for in 17 samples. Subsamples (111) representing each core section were sealed in plastic sample boxes and stored in fiberglass

Table 1
Sample locations, core lengths and water depths, Voronin Trough cores collected during July–August, 1965

Core ID	Latitude	Longitude	Core length (cm)	Depth (m)
15	80°36′N	87°39′E	91	302
16	81°04′N	87°31.9′E	96.5	332
17	81°27.5′N	97°34′E	93	265
18	81°30.5′N	87°38.8′E	107	399
19	81°30.5′N	84°53.5′E	93	405
20	81°32.7′N	82°18′E	95	315
21	81°34.8′N	79°51.8′E	90	205
29	81°08′N	82°05′E	58	663
30	81°07′N	83°58′E	76	300
31	80°35.8′N	83°59′E	78	307
32	80°00.5′N	89°00.5′E	102	200
33	79°35.5′N	84°02′E	117	208
34	80°41.1′N	82°13′E	82	206

containers at room temperature until they were reclaimed for this project.

3.2. Laboratory

Chemical analyses were done by ICP-AES after a 4 acid nearly total digestion (Al, Cd, Cu, K, Mg, Mn, Mo, Ni, P, Pb, Sr, Ti, V and Zn), INAA (As, Cr and Fe), and cold vapour AAS (Hg). USGS GXR-1, -2 and -4 standards were used to check accuracy for the ICP-AES data and CANMET standards SO-2 and MGR were used for the INAA and AAS data. Coefficients of variation for 16 replicate analyses in the suite of 111 samples were <5% for Al, Cu, Hg, K, Mg, Mo, Ni, P, Sr, Ti, V and Zn, 5–10% for As and Mn, and 10–15% for Cd (only 20 samples above detection limit) and Pb. Size analysis was done by sieving and pipette analysis

3.3. Statistical

Cluster analysis was done to reveal significant associations among the variables that assist in making a fuller explanation of the physical and geochemical processes active in determining the chemistry of the sample suite. The analysis is designed to perform classification by assigning observations to groups so that each group is more or less homogeneous and distinct from other groups. In this study cluster analysis places elements/size data into more or less homogeneous groups (communality) in a manner so that the relation between groups is revealed. Hierarchical clustering joins the most similar observations, then successively connects the next most similar observations to these (Davis, 1986). Factor analysis was used to indicate the quantitative influence of associated variables on the variation in the geochemical-granulometric data set.

When element concentrations within a core were evaluated for contaminant enrichment, they were normalized to the conservative element Al. Normalization was done by dividing the element concentration in a sample by its Al% value. This diminishes the influence of changes in texture on sediment geochemistry (Bifano and Mogollon, 1995). Clay-size and silt-size detritals comprise >57% and >35% of the sediment, respectively.

4. Results and discussion

For most of the elements studied, concentrations are relatively consistent within and among cores. This is indicated by relatively small standard deviations (Table 2). However, Hg and As, and Mn and P have large standard deviations (>50% of the mean) caused

Table 2

Descriptive statitics for geochemical parameters of 111 samples from the Voronin Trough, Kara Sea, Arctic Ocean, with comparative data from Novaya Zemlya Trough cores for 86 samples (after Lee et al., 1996). Values are in ppm unless otherwise noted[a]

	Voronin Trough				Novaya Zemlya Trough			
	x	c.v.	Min	Max	x	c.v.	Min	Max
Al%	7.60	1.18	3.05	9.45	7.5	0.7	3.0	8.8
As	34	37.5	8.8	270	47.1	52.6	9.5	240
Ca%	0.81	0.49	0.28	3.38	0.7	0.2	0.3	1.6
Cd[b]	0.7	0.4	BDL	2.1	0.6	0.3	BDL	2.0
Co	23	7.4	8	52	27.9	6.7	15	50
Cr	117	18.2	60	180	102	10.8	78	127
Cu	28	7.5	6	52	31.4	9.7	18	86
Fe%	4.97	1.09	1.59	10.2	5.0	0.8	3.3	7.8
Hg ppb	442	350	75	2045	385	157	195	875
K%	2.08	0.26	1.35	2.58	2.6	0.3	0.9	2.9
Mg%	1.33	0.23	0.36	1.63	1.5	0.2	0.6	1.9
Mn%	0.11	0.18	0.03	1.27	0.4	0.6	0.04	2.8
Na%	1.95	0.4	1.11	3.51	2.2	0.3	1.4	3.0
Ni	52	11.3	16	80	50.2	7.6	29	64
P%	0.1	0.05	0.03	0.37	0.1	0.1	0.05	0.3
Pb	18	4.2	10	34	17.5	4.4	7	25
Rb	98	24.4	10	170	96.4	16.8	12	135
Sb	1.2	0.5	0.4	3.2	2.5	1.1	0.6	6.4
Sc	17	2.7	6.1	2.2	15.4	1.3	12.6	19.1
Sr	145	29.5	85	329	139	24.3	73	219
Th	8.3	1.2	3.7	11	8.3	0.8	6	10.2
Ti%	0.42	0.05	0.22	0.52	0.4	0.04	0.2	0.5
V	208	41.5	63	304	176	32.6	71	223
Zn	102	20.8	28	209	91.4	10.5	64	110

[a] x = average concentration; c.v. = coefficient of variation; Min = minimum value; Max = maximum value; BDL = below detection limit.

[b] Voronin trough for 20 samples at or above detection limit Novaya Zemlya Trough for 43 samples at or above detection limit.

by very high contents in surface/near-surface samples of several Voronin Trough cores compared to baseline (natural) values deeper in the cores.

Some Hg values are much greater (to 2045 ppb) than those reported by Galasso et al. (2000) for Novaya Zemlya Trough sediments (to 875 ppb). Arsenic has high concentrations of 200 and 270 ppm in two cores which are similar to high values (212 and 240 ppm) in Novaya Zemlya Trough cores. Table 2 summarizes the descriptive statistics of the chemical elements studied and gives comparative data from Novaya Zemlya Trough cores. Table 3 gives cores' granulometry.

4.1. Distribution within cores

The cores range in length from 58 to 107 cm. On the basis of the range for sedimentation rates reported by Forman et al. (1996) for the Kara Sea (0.1–1.0 mm/y), the top 4 cm can represent a minimum of 40 a to a maximum of 400 a. With respect to the sampling in 1965, even the minimum time

Table 3

Size distribution in cores from the Voronin Trough, Kara Sea. Values are in weight percent

	Gravel[a]	Sand	Silt	Clay
Core 15	0.14	10.27	36.05	53.54
Core 16	0.16	9.02	33.86	56.96
Core 17	0.33	18.32	26.78	54.57
Core 18	t	5.11	28.03	66.81
Core 19	t	1.07	40.38	58.55
Core 20	t	4.82	33.94	61.20
Core 21	0.78	10.41	45.76	43.05
Core 29	0.48	18.50	40.84	40.18
Core 30	t	2.72	38.28	58.99
Core 31	0	1.54	29.73	68.73
Core 32	t	3.82	32.97	63.20
Core 33	t	2.79	32.33	64.84
Core 34	t	4.52	45.20	50.25

[a] t = trace (< 0.05).

represents pre-industrialized Siberia. Deeper sections in the cores (e.g., 20 cm representing 200–2000 a) should reflect global pre-industrialization and hence natural chemistry for the cores. Industrialization in the region began in about 1934. With a more limited sedimentation rate range of 0.2–0.6 mm/a for waters greater than 200 m deep (Forman et al., 1996), heavy metal contamination from Siberian sources and the Urals in these cores collected in 1965 should be found in the top few centimeters. This assumes that no physical, chemical or biological process has mobilized chemical elements to deeper or to upper core sections. This assumption may not always be valid as explained below.

Mercury concentrations > 1000 ppb were found in 7 of 13 cores studied. These high values were present in surface samples to 5 cm deep (Cores 20 and 33; Fig. 4) and in near-surface samples generally less than 20 cm deep (e.g., Cores 15, 19, 30 and 32; Fig. 4). Enrichment factors (concentration maxima divided by natural baseline values) range from

≈7 (Cores 33 and 30; Fig. 4) to little or none (Cores 18 and 21; Fig. 4). The enrichment is attributed to anthropogenic activities.

Arsenic also had high concentrations in surface/ near-surface samples up to a depth of about 20 cm (Fig. 5). Enrichment factors range from 20 (Core 19) to ≈2 (Core 18) or less. This is attributed to diagenesis by chemical mobilization of natural As contents from within cores under reducing conditions towards surface/near-surface sections with oxidizing conditions, as well as to anthropogenic loading.

In some samples high Hg and As concentrations seem to follow each other (e.g., Cores 33, 19 and 15; Figs. 4 and 5) but in other samples they do not (e.g., Cores 16 and 17; Fig. 6). The observation that both Hg and As high values reach depths representative of regional or global pre-industrialization times (i.e., > 4 cm) suggests that other factors affect their distributions.

One factor is bioturbation which was recognized by Young (1996, pers. comm.) in radiographs as tracks
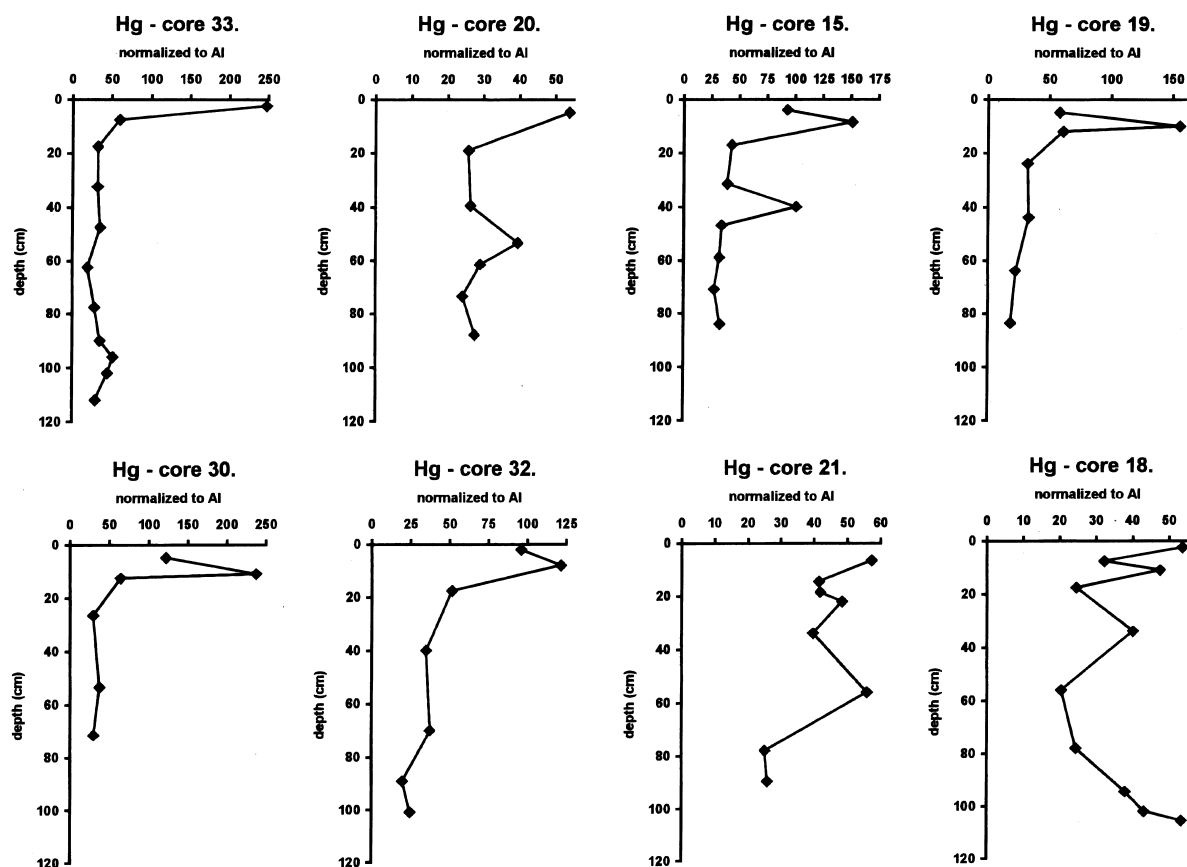

Fig. 4. Examples of downcore profiles of Hg ppb concentrations normalized to Al percent.

and burrows (e.g., from pogonophorans) extending to about 20 cm in Kara Sea cores collected during 1992. This mixing redistributes metals concentrated in the surface sediments to the upper ≈ 20 cm sequence. The redistribution dilutes the surface sediment values and suggests that surface sediment may have had greater heavy metals contents when deposited than the maximum values measured in the bioturbated core sections.

A second factor that could affect As distribution in cores but not that of Hg is electro-chemical. At depth in marine cores, reducing environments may reach Eh levels that can mobilize As as the arsenite anion complex ($HAsO_4^{2-} - As^{3+}$). The arsenite will migrate upward in the sediment sequence until it reaches oxidizing conditions that cause arsenate ($HAsO_4^{2-} - As^{5+}$) to form. The arsenate can attach to charged surfaces such as Fe oxy/hydroxides. Selective extraction in eight samples of Kara Sea trough sediments show a strong covariance with an amorphous Fe oxy/hydroxide phase ($r = +0.74$ for the As-Fe pair). In time, this pro-
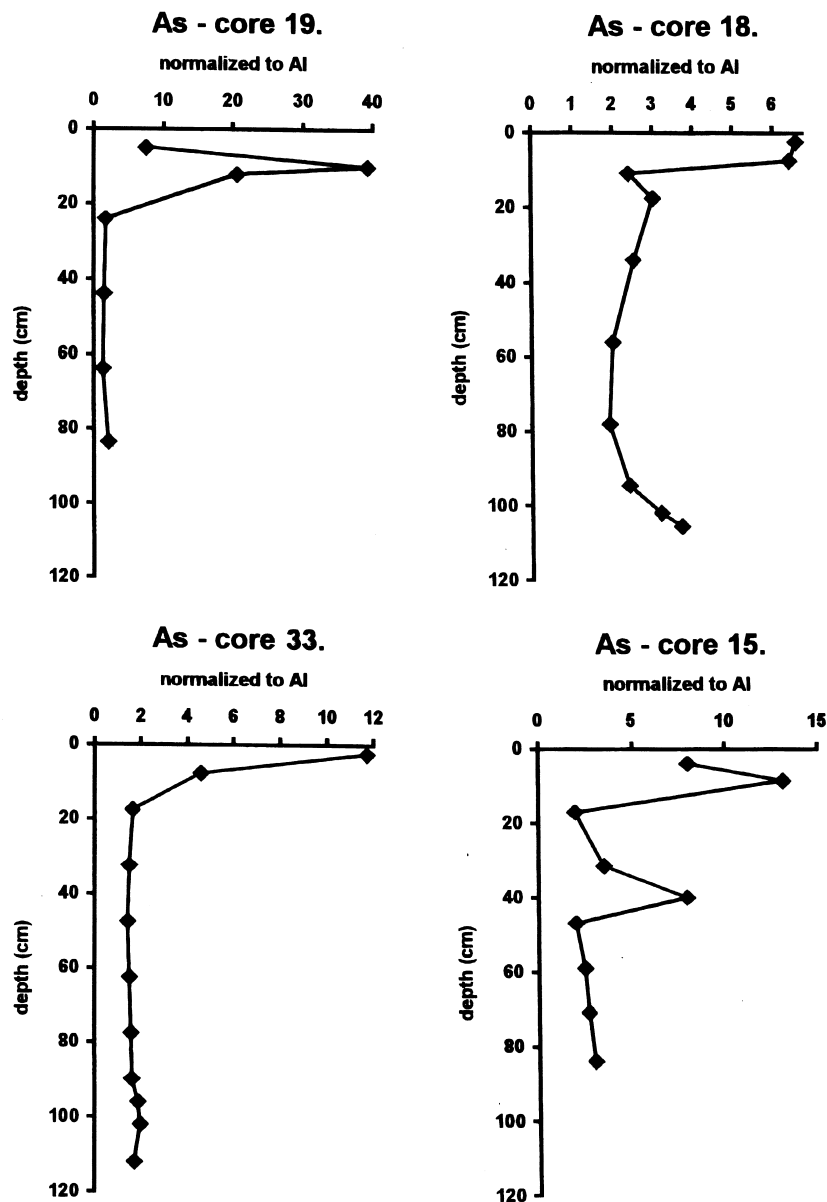

Fig. 5. Examples of downcore profiles of As ppm concentrations normalized to Al percent.

cess can add high natural As contents to anthropogenic contamination from industrial activities or, conversely, anthropogenic contaminant can be added to high natural diagenesis influenced As contents. With arsenate in the system, electro-chemistry suggests that as electrons are released when arsenite transforms to

arsenate, there can be a reduction of Mn^{4+} to Mn^{2+}. The Mn^{2+} can then be mobilized upward in the sediment section to deposit as Mn^{4+} oxy/hydroxides where oxidation conditions permit, often in surface sediments above As maxima. This is the case in Voronin Trough cores (e.g., Core 15, 17, 19; Fig. 7).
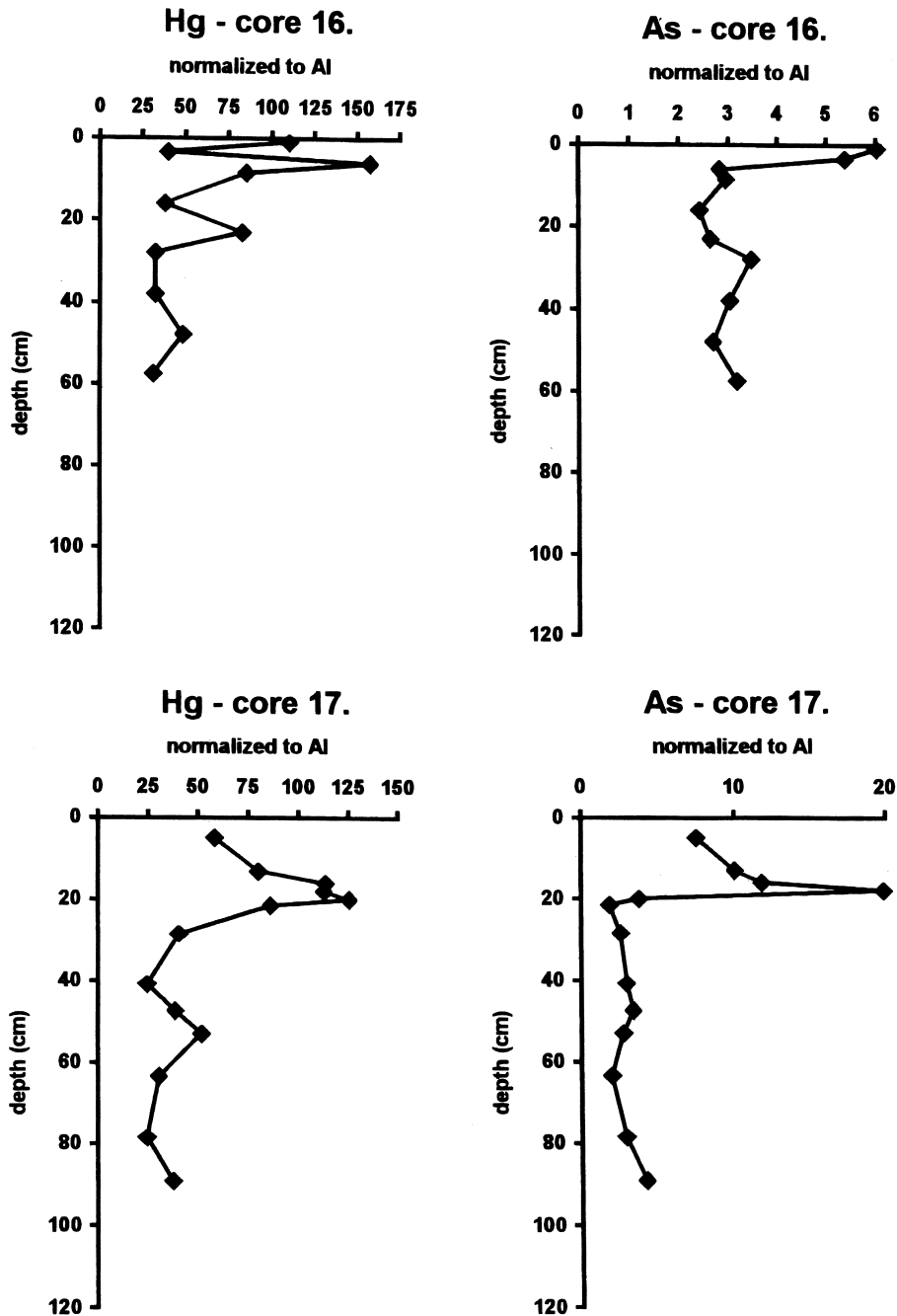

Fig. 6. Comparison of downcore profiles for Hg ppb and As ppm normalized to Al percent showing similar distribution patterns.

4.2. Distribution between cores

4.2.1. Mercury

Much of the Hg in Voronin Trough sediments probably originates in atmospheric emissions from smelt-

ing/refining of sulfide ores, from incineration of Hg-bearing industrial wastes and from burning of fossil fuels (especially coal). Pirrone et al. (1996) reported that coal combustion is a source of about 40% of atmospheric Hg in the former USSR. Mercury vapor
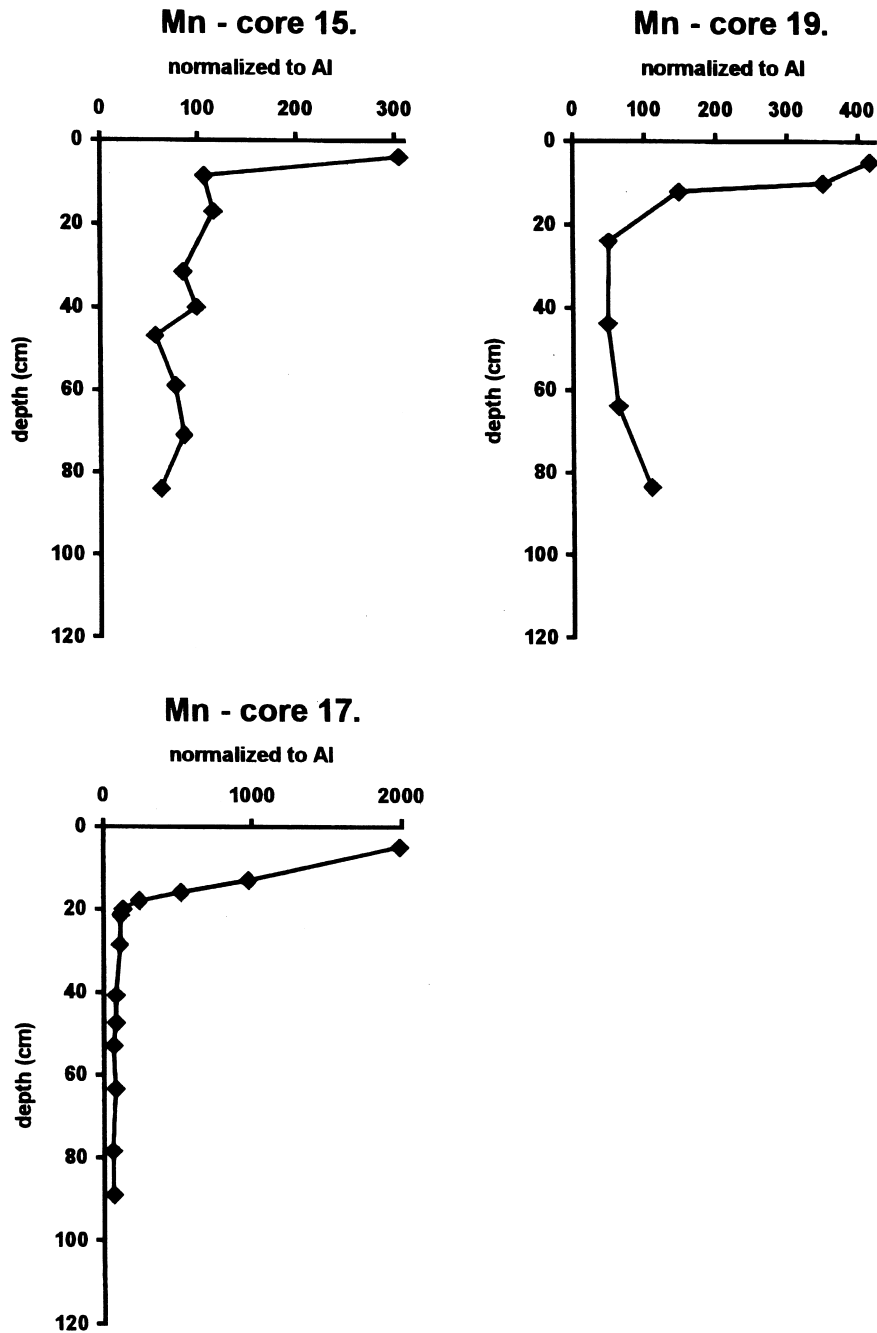

Fig. 7. Downcore profiles of Mn ppm concentrations normalized to Al percent. A comparison with Figs. 5 and 6 shows that Mn maxima are higher in the section than As maxima.

may be airborne 3 months to 3 a and transported long distances by prevailing winds before being deposited (AMAP, 1997; Pacnya, 1995). Coquery et al. (1995) calculated that atmospheric deposition accounts for 2650 kg/a of Hg deposited annually in the Kara Sea but did not account for Hg deposited on the catchment area and carried in runoff to the sea. Mercury-bearing effluents from Siberian industries such as chlor-alkali and pulp and paper manufacture plants flow into streams and rivers that discharge in the Kara Sea. Recently, Koval et al. (1998) found 2.5–8000 ppb Hg vs a background of 480 ppb in sediment from the reservoir behind the Bratsk hydroelectric dam in the upper basin of the Angara River (Fig. 1). This river is a principal tributary to the Yenisey River. Mercury originated in effluents from chemical industries, and in runoff from agricultural pesticides and Au amalgamation (from placer mining). The Bratsk dam was completed in 1964. Input of Hg to the Angara River before 1964 would have entered the Yenisey River

drainage system carrying Hg to the Kara Sea and could have contributed to the high Hg contents in the cores collected in 1965. Although there is no reported Hg mining in the Siberian area linked to the Kara Sea, a middle Ob latitudinal Hg zone (Fig. 1) was described by Lukin and Garipov (1994). There is so much Hg vapour accompanying gas and gas-condensate extracts there, that native metal precipitates. Mercury was not recovered and was presumably released into a tributary of the Ob river.

In fluvial systems Hg may be mobilized as the free ion or adsorbed onto clay minerals or particulate organic matter. It may undergo biomethylation by life forms in the food web and bioaccumulate. However, in the estuaries of the Yenisey and Ob rivers there is a negative correlation between suspended particulate organic matter and Hg (data from Coquery et al., 1995). This indicates that organic matter does not influence Hg distribution in the estuaries.

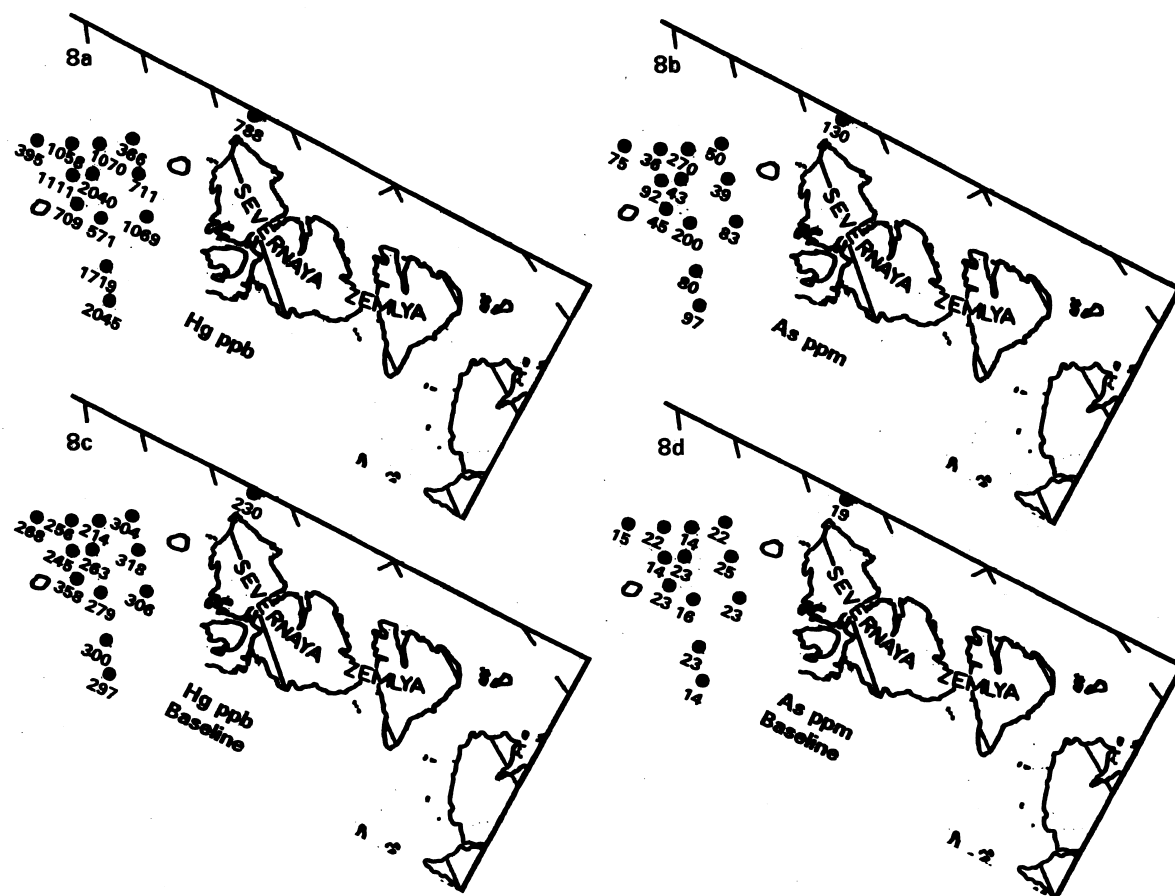In ocean water Hg can be mobilized as Hg^{2+} and

Fig. 8. Regional distribution of Hg (a) and As (b) high values in Voronin Trough cores with corresponding baseline contents for Hg (c) and As (d) in the cores.

$HgCl_4^{2-}$, and may undergo biomethylation by phytoplankton and algae, for example, and bioaccumulate as the toxic methyl Hg (CH_3Hg^+). This can move up the food web to higher life forms. Joiris et al. (1995) reported an average Hg background of 340 ppb for European Arctic Seas from a suite of 12 suspended sediment samples from the Barents Sea (between Franz Josef Land and Svalbard) and from the Greenland Sea between Svalbard and Greenland. Joiris et al. (1995) found that only 2% of the Hg was methylated and that there was a negative correlation with C_{org}. In the south Kara Sea, however, there was a positive correlation between Hg and suspended particulate organic matter (Coquery et al., 1995). In the present study, C_{org} ($X = 1.4\%$; $n = 17$) had a weak invariant correlation with Hg.

Fig. 8(a) gives the distribution of the high Hg values in Voronin Trough cores' surface/near-surface samples. Fig. 8(c) presents the baseline values for Hg from samples in deeper sections of these cores. The relation of distribution patterns to ocean currents that likely transported Hg-bearing suspended sediments along well-defined flowpaths for deposition in the trough can be evaluated using Fig. 3.

Of the 13 sampling sites in the trough, two have samples with Hg values > 2000 ppb and another 5 have values > 1000 ppb. These values are much higher than the average Hg content in trough sediments (442 ppb, Table 2) or the average baseline concentration of 279 ppb Hg. However, they are similar to Hg values of 1880 ppb, 1800 ppb and 1670 ppb reported by Coquery et al. (1995) for total suspended particulate matter in the Laptev Sea east of Severnaya Zemlya. The origin of Hg in Laptev Sea suspensates is attributed to a combination of atmospheric deposition, erosion, and transport of particulates by the Lena River that empties into this sea (Coquery, pers. comm., 1997). Mercury is also likely being discharged from placer Au mining in the Lena River drainage basin.

Another possible source of Hg in Laptev Sea suspended sediments that can also influence sediment carried to the Voronin Trough may be related to the Western Taimyr Current. This current transports sediment discharged into the Kara Sea across the Ob-Yenisey delta (Fig. 3). Mercury in suspensates sampled along the flowpath towards the Western Taimyr Current increased in concentration from 40 to 240 ppb in surface and intermediate depth water masses to 420 ppb and 670 ppb in intermediate and deep water masses (Coquery et al., 1995). There is additional input to the current from the Pyasina River watershed which drains an area that includes the largest point sources for toxic metal emissions in the world (smelters in the Norilsk area — Fig. 1). Mercury from these and other emissions (e.g., from the burning of fossil fuels in electricity generating plants and for heating), plus atmospherically deposited Hg from eroded soils can be carried by streams to the river. Added to this is Hg from Norilsk industrial effluents and from placer Au mining in the river watershed that can be transported by the Pyasina River and discharged into the Kara Sea. Much of this river load likely enters the Western Taimyr Current. The current with its entrained sediment or sediment particles adhered to pack ice flows northeastward and branches south of Severnaya Zemlya (Fig. 3). One branch flows to the east towards the Laptev Sea. The other branch flows to the NW to the Voronin Trough. High Hg contents measured in the trough sediments may originate in part with the Western Taimyr Current system and thus represent metal loading from the Yenisey and Pyasina rivers.

4.2.2. Arsenic

Like Hg, much of the As in the drainage basins discharging into the Kara Sea probably originates as atmospheric deposition of heavy metal-bearing emissions. Arsenic also enters these catchments as leachate from mine tailings and as runoff from fields treated with pesticides (Yablokov, 1996). Effluents from industrial complexes in the Urals and Siberia (e.g., chemical plants, cement production) can also contribute to the fluvial As load. The element is mobile under all conditions likely in the natural environment either as the arsenite ($HAsO_3^{2-} - As^{3+}$) or the arsenate species ($HAsO_4^{2-} - As^{5+}$) depending on redox potential and pH (Hale, 1981). When an arsenite ion enters sea water with a pH of ~ 8.1, it alters to arsenate. In sea water, arsenate originating in river discharge as arsenite or arsenate, is adsorbed onto Fe oxy/hydroxide particulates and transported by ocean currents in the suspended load or adhered to pack ice moving with the currents to depositional environments. The phosphate ion in sea water competes with the arsenate ion for sorption onto Fe oxy/hydroxides. This is reflected in a strong positive statistical cluster of P with Fe and As (Fig. 9).

On average, fine-size marine sediment contains about 17 ppm As (Chester, 1989). Values greater than 100 ppm have been reported in coastal areas polluted by mining and/or industrial wastes. Surface/near-surface sediments with values from 112 to 212 ppm As were reported for 6 of 8 cores from the Novaya Zemlya Trough (Galasso et al., 2000). At the 13 sites sampled in the Voronin Trough, there is a high As content of 200 ppm in the center. Another core more to the north in the trough has a value of 270 ppm As. The distributions of high As values in surface/near-surface sediment in the cores and of baseline As values analysed in deeper core samples are given in Fig. 8(b) and (d). High values in other cores are less than 100 ppm, still indicating As contamination when compared with an average of 34 ppm As for Voronin Trough

sediments (Table 2) or the average baseline value for trough sediments of 19 ppm As. Heavy metals were analysed in sediments and waters in the Ob and Yenisey estuaries and the southern Kara Sea collected during research cruises in the early 1990s (Fuhrmann and Dyer, 1996; Gurvitch et al., 1995; Loring et al., 1995, 1997) but they did not report on As and/or Hg contents. The upper 2 cm of one core sample in the Kara Sea area influenced by discharge and current

flow fom the Ob River had 140 ppm As (Loring, per com, 1997).

In addition to the association of As, P and Fe cited above, Fig. 9 has a cluster that suggests a strong correlation among clay size sediment, elements comprising aluminosilicate detritals, and metals probably adsorbed onto them. A Ca-Sr cluster is likely due to plagioclase which is present in the clay size fraction (authors' unpublished data) whereas the Mn-Co cluster possibly
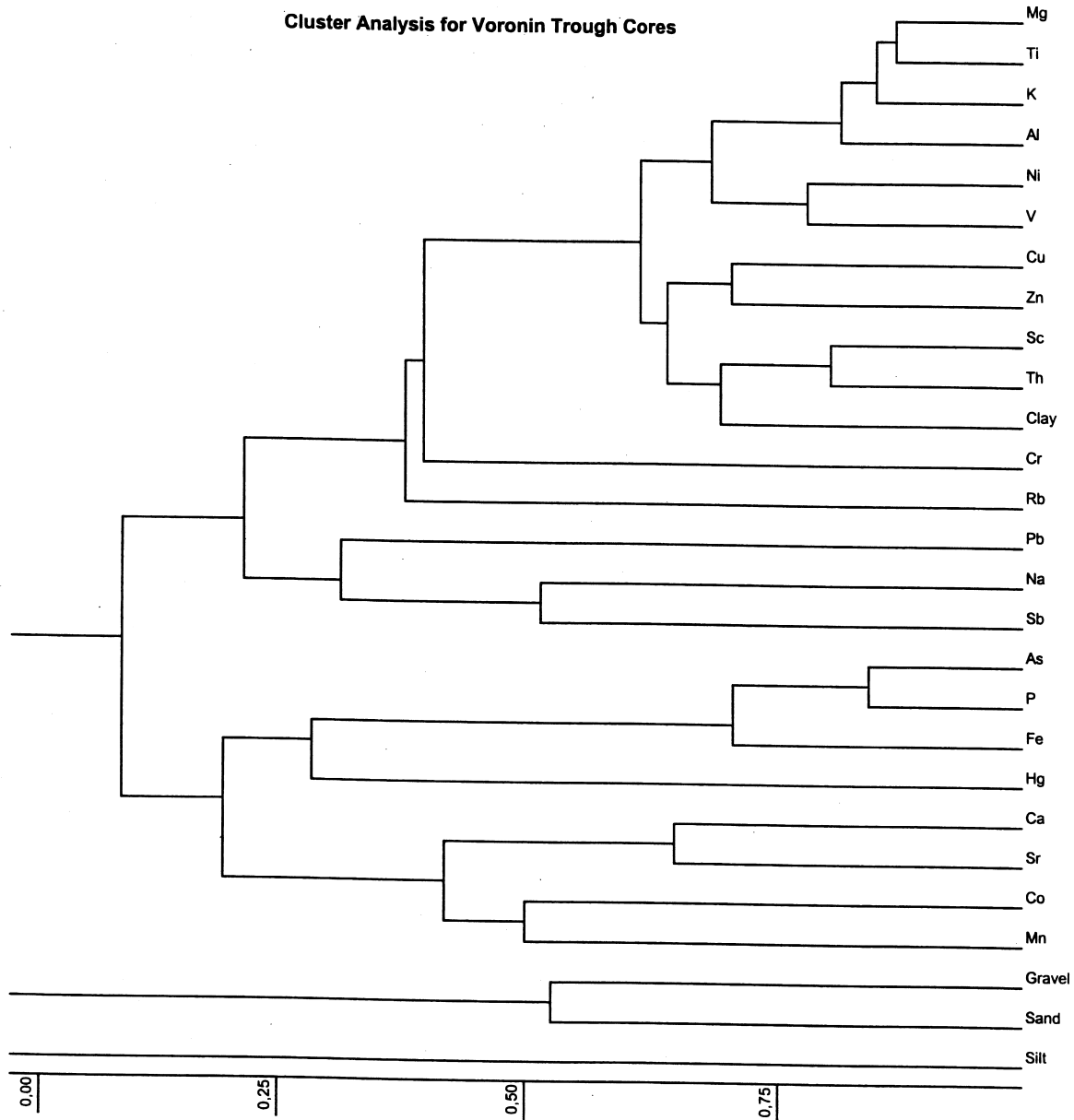

Fig. 9. Cluster analysis for the geochemical-granulometric data set.

reflects sorption of Co onto Mn oxy/hydroxides. Factor analysis revealed groupings of variables that have a good correspondence with the clusters. The dominant factor represents the clay-size aluminosilicates and adsorbed metals, followed by a second factor of As, P and Fe, and a third factor comprised of Ca-Sr and Mn-Co. These account respectively for 36, 18 and 8% of the variance in the geochemical-granulometric dataset.

The fact that sampling in the estuaries of the Ob and Yenisey rivers and on the delta formed by the rivers yielded no high value samples for As that could indicate provenance of anthropogenic As contaminants may be a result of the timing of sampling. Sampling was done after June and was undoubtedly affected by the massive flood discharge to the estuarine-delta complex and parts of the southern Kara Sea. The samples in the estuaries may represent samples from which fine-size fractions had been resuspended into the water column so that heavy metals signals would probably not be preserved or the samples may be from areas of scouring and erosion from where As and heavy metal bearing sediment has been moved to other depositional environments in the sea. Also, an increase in larger size sediment fractions (silt and sand) composed of quartz and feldspar and added to clay-size sediment during flood stage carry little of the metals being evaluated. This would dilute the chemical signal from As and potentially toxic metals. As cited previously, suspended sediment samples in the study area contained high values of 420 and 670 ppb Hg (Coquery et al., 1995). These samples were collected during September after the major discharges from the Siberian watersheds. Unfortunately, As was not determined in these suspensates.

It was suggested above that As contamination likely originates from atmospheric emissions and deposition, and runoff from mine tailings and agricultural areas, mainly from sources in Siberia and the Urals. Input from smelting/mineral processing and industrial sources on the Kola Peninsula probably adds to the As loading. Arsenic-bearing fine-size sediments discharged by the Yenisey and Pyasina rivers can reach the Western Taimyr Current (Fig. 3) which transports them for deposition in the Voronin Trough in much the same way as Hg. Areal distribution may also be influenced by the size and/or density of the transporting phases. The dispersion of Hg (Fig. 8(a)) probably sorbed onto clay minerals (SG = 2.7) or particulate organic matter is greater than that of As (Fig. 8(b)) sorbed onto Fe oxy/hydroxides.

5. Pollution potential of Hg and As

Arctic coastal birds, the ringed seal (the principal food source for the polar bear), and the polar bear have higher than normal contents of Hg and As in body organs and muscles (Muir et al., 1992; Norheim et al., 1992; Savinova et al., 1997). These higher concentrations may originate in the marine food web as suggested below.

Mercury in the sedimentary sequence is immobile in the presence of the sulfide ion over a wide range of pH. It may be deposited as an adsorbed ion (Hg^{2+}) or ion complex ($HgCl_4^{2-}$) on a charged surface of clay minerals such as a smectite or kaolinite and/or on organic particulates. It can also be accumulated by marine life as a biomethylated (CH_3Hg^+) species and be mobilized up the food web in this form.

There is little likelihood of chemical mobilization of As from marine sediments in oxidizing surface/near-surface sedimentary environments. Physical mobilization by mass movement from the sides of the trough to deeper levels can displace As-bearing sediment as can bioturbation mixing of surface with near-surface sediments. However, neither process stimulates chemical migration that allows an As anionic complex to access the food web. It is possible, however, that bottom feeders passing sediment through their systems to access nutrients can extract and bioaccumulate As (and Hg). When these feeders are consumed along the food web there can be a bioaccumulation carried through to the higher life forms cited above.

6. Conclusions

Kara Sea sediments deposited in the Voronin Trough prior to August–September 1965 have contaminant levels of Hg and As. The high contents of these elements relative to pre-industrial (baseline) contents at depth in cores are generally found in the upper ~20–30 cm of cores. This is deeper than expected on the basis of estimated sedimentation rates and the start of industrial activities in areas that could be sources of As and Hg. Bioturbation has likely mixed the sediment. Arsenic mobilization upward under reducing conditions can add a natural loading to oxidized surface/near-surface sediment anthropogenic contents but Hg will be immobile under these conditions.

In addition to input from natural sources, Hg and As entered the marine environment pre-1965 from anthropogenic sources in Siberia, the Urals and perhaps the Kola Peninsula. This input may continue today (Yablokov, 1996). The sources likely include emissions (e.g., from smelting/mineral processing and burning of fossil fuels for electrical generation and heating) followed by atmospheric deposition, industrial effluent discharge, drainage from mining operations, dumped military materials and incinerated wastes. Mercury and As are transported on particulates to the

trough by marine currents and pack ice where they are differentially deposited according to size and specific gravity of the substrate materials carrying them.

The potential for mobilization of Hg and As from surface/near-surface marine sediment in the Voronin Trough is limited by chemical conditions. However, bottom feeders that extract nutrient from sediment may extract the Hg and/or As and pass them up the food web. Coastal birds, ringed seal and polar bear have been found with moderately high levels of Hg and/or As in their bodies.

To approximate how much of the Hg and As marine sediment inventory has sources in Siberia and the Urals requires a more definitive type of sampling than was done in the estuaries and on the Ob-Yenisey delta during the 1990s after heavy summer river discharge. Overbank and floodplain core samples from the Ob, Yenisey and Pyasina rivers can reveal the history of anthropogenic Hg and As deposition in their drainage basins and the Kara Sea.

Acknowledgements

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